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The Inorganic–Organic Hybrid Compound $\{[Mn(trien)]_2SnS_4\}\cdot 4H_2O$: Exhibiting a Hitherto Unknown Binding Mode of the $[SnS_4]^{4-}$ Tetrahedron

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The compound $\{[Mn(C_6H_{18}N_4)]_2SnS_4\}\cdot 4H_2O$ ($C_6H_{18}N_4$ = triethylenetetramine) was obtained under solvothermal conditions. In the structure of the $\{[Mn(C_6H_{18}N_4)]_2SnS_4\}_\infty$ chain, two S atoms of the $[SnS_4]^{4-}$ anion act in a hitherto never observed μ_3 bridging mode that connects the $Mn_2S_2N_8$ di-octahedra. The Mn^{2+} ions are octahedrally coordinated by four N and two S atoms, and two symmetry-related octahedra share a common S–S edge. Three of the H_2O molecules are joined into chains through H-bonding interactions.

Thiostannates are an attractive group of compounds among the main group thiometalates, and some of them show zeolite-like properties. Some materials with interesting structural features and properties were prepared under solvothermal conditions. The Sn^{II}/Sn^{IV} ions exhibit a flexible coordination behavior, and typical polyhedra are SnS_3 trigonal pyramids, SnS_4 tetrahedra, SnS_5 trigonal bipyramids, or SnS_6 octahedra. Different connection modes of these primary building blocks lead to the formation of discrete molecules, 1D chains, or 2D layered structures. Compounds with the $[SnS_4]^{4-}$ monomer are known, but more often the $[Sn_2S_6]^{4-}$ di-tetrahedron is found in thiostannates.[1,2] The integration of transition metals (TM) into the thiostannate networks alters the physical and chemical properties of such compounds, and some of these compounds have interesting properties for different applications.[3,4] Until now, several TM thiostannates were reported, reflecting the variable and flexible connection modes of the building units. Recently, we published the structures of the new copper and manganese thiostannates (DBUH)$CuSnS_3$ (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene), $(1,4\text{-dabH})_2Cu_2SnS_4$ (1,4-dab = 1,4-diaminobutane),[5] and $(1,4\text{-dabH}_2)MnSnS_4$[6] with SnS_4 tetrahedra and Cu^+/Mn^{2+} as part of the anionic chains. In $(enH_2)HgSnS_4$, the $[HgSnS_4]_\infty$ columns consist of SnS_4 tetrahedra and HgS_3 triangles.[3] The 2D compound (enH_2)-Ag_2SnS_4 contains $[Ag_2SnS_4]^{2-}$ layers with SnS_4 tetrahedra, in which each S atom bonds to AgS_2 dumbbells to form twisted chains.[7]

Most of the thiostannates formed under solvothermal conditions are composed of transition-metal complexes $[TM(amine)_x]^{y+}$ as charge-compensating cations for the $[Sn_2S_6]^{4-}$ anions, e.g. in $[Ni(en)_3]_2Sn_2S_6$ (en = ethylenediamine), $[Ni(dap)_3]_2Sn_2S_6\cdot 2H_2O$ (dap = 1,2-diaminopropane),[8] $[M(en)_3]_2Sn_2S_6$ (M = Mn, Co, Zn),[9] $[Ni(en)_3]_2$-Sn_2S_6, $[Ni(dien)_2]_2Sn_2S_6$, (dien = diethylenetriamine),[10] $[Mn(en)_3]_2Sn_2S_6\cdot 2H_2O$, $[Mn(dien)_2]_2Sn_2S_6$,[11] and $[\{Mn(en)_2\}_2(\mu\text{-en})(\mu\text{-}Sn_2S_6)]_\infty$.[12] Very recently, the first thiostannates with lanthanide-containing cations were reported,[13,14] but even here $[Sn_2S_6]^{4-}$ anions are observed. Herein, we present the new thiostannate $\{[Mn(trien)]_2$-$SnS_4\}\cdot 4H_2O$ (trien = triethylenetetramine, $C_6H_{18}N_4$). The compound features SnS_4 tetrahedra connected with di-octahedral $Mn_2N_8S_2$ units in a novel coordination mode.

$\{[Mn(trien)]_2SnS_4\}\cdot 4H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell and all atoms located on general positions. The structure consists of neutral $\{[Mn(trien)]_2SnS_4\}_\infty$ chains running along [001] and water molecules. A section of a chain is depicted in Figure 1. The Sn–S distances in the SnS_4 tetrahedron in the range 2.3736(9)–2.4275(9) Å and S–Sn–S angles in the range 102.21(3)–111.71(3)° (Table 1) indicate a moderate deviation from ideal tetrahedral geometry. These values match well with data published in literature.[8,17] The Mn^{2+} cations are sixfold-coordinated by four N atoms of the triethylenetetramine and two S atoms of two SnS_4 tetrahedra. In the octahedra, two N and two S atoms form the base and two further N atoms are at the apices. Hence, a severe distortion is observed and is evidenced by the Mn–S/Mn–N bond lengths that scatter over the range 2.5359(11)–2.7115(10)/2.259(3)–2.370(3) Å as well as by the N–Mn–N/S–Mn–N angles (Table 1). Two symmetry-related MnN_4S_2 octahedra share a common edge, and the resulting building units may be represented as $Mn(1)_2S_2N_8/Mn(2)_2S_2N_8$ di-octahedra (Figure 2). Because of edge sharing, the Mn^{2+} ions are significantly shifted away from the centers of the octahedra, which gives rise to the observed strong distortion. The Mn–N/S bond lengths are in the range reported in similar structures in the literature.[11,12,18,19] We note that com-

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pounds with $Mn_2S_2X_8$ dioctahedra are known, but only as discrete molecules, such as in $C_{18}O_{16}Mn_4S_6$[20] or $C_{20}H_{10}Mn_2O_8S_2$,[21] and not as a structural motif in extended structures. Whereas two S atoms of the $[SnS_4]^{4-}$ anion [S(3) and S(4)] are terminal, S(1) and S(2) act in a μ_3 binding fashion, each having bonds to two symmetry-related Mn^{2+} ions, i.e. these two S atoms join two di-octahedra. Therefore, the compound may be viewed as a 1D inorganic–organic hybrid compound in which the di-octahedra are the nodes and the $[SnS_4]^{4-}$ anions are the linkers.

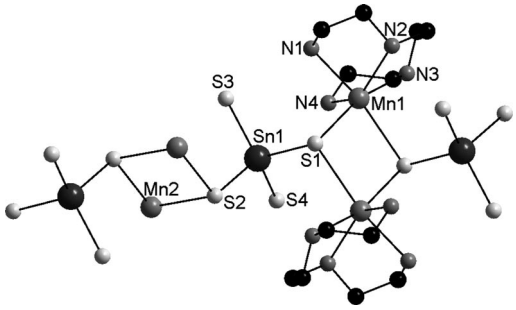

Figure 1. Binding mode of the $[SnS_4]^{4-}$ tetrahedron with the di-octahedra. The H atoms of the amine molecules and the amine molecules of Mn2 are omitted for clarity.

Table 1. Selected bond lengths, angles, and geometric parameters indicating hydrogen-bonding interactions.

Sn–S	Distance [Å]	S–Sn–S	Angle [°]
Sn–S1	2.4275(9)	S1–Sn–S2	102.21(3)
Sn–S2	2.4070(10)	S1–Sn–S3	111.49(3)
Sn–S3	2.3736(9)	S2–Sn–S3	111.71(3)
Sn–S4	2.3782(10)	S1–Sn–S4	110.50(3)
		S2–Sn–S4	109.05(3)
		S3–Sn–S4	111.50(3)
Mn–N/S	Distance [Å]	N/S–Mn–N/S	Angle [°]
Mn1–N1	2.317(3)	N4–Mn1–N1	82.90(13)
Mn1–N2	2.370(3)	N3–Mn1–N1	107.90(12)
Mn1–N3	2.315(3)	N4–Mn1–N3	76.67(13)
Mn1–N4	2.271(3)	N4–Mn1–N2	134.10(12)
		N3–Mn1–N2	74.09(12)
		N1–Mn1–N2	73.56(12)
Mn1–S1	2.5874(11)	S1–Mn1–N1	86.95(9)
Mn1–S1[a]	2.7115(10)	S1–Mn1–N2	113.56(9)
		S1–Mn1–N3	164.98(9)
		S1–Mn1–N4	103.64(9)
Mn2–N5	2.259(3)	N5–Mn2–N6	77.38(13)
Mn2–N6	2.298(3)	N5–Mn2–N7	148.79(13)
Mn2–N7	2.299(3)	N6–Mn2–N7	76.20(12)
Mn2–N8	2.341(3)	N5–Mn2–N8	89.47(13)
		N6–Mn2–N8	93.69(13)
		N7–Mn2–N8	76.00(12)
Mn2–S2	2.5359(11)	S2–Mn2–N5	110.71(10)
Mn2–S2[a]	2.6581(11)	S2–Mn2–N6	170.20(9)
		S2–Mn2–N7	97.45(9)
		S2–Mn2–N8	91.94(9)
S···H–O/N	Distance [Å]	Angle [°]	S···O/N Distance [Å]
S1[b]···H–O1	2.448	159	3.2943
S2[b]···H–N3	2.870	158	3.7297
S3···H–N1	2.610	153	3.4373
S3···H–N4	2.848	154	3.6801
S3···H–O4	2.355	167	3.3101
S4···H–O1	2.388	173	3.1944
S4···H–O4	2.382	163	3.1628
S4···H–N2[b]	2.505	148	3.3085
S4···H–N8	2.560	163	3.4321

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$. [b] : $-x + 1, -y + 1, -z + 2$.

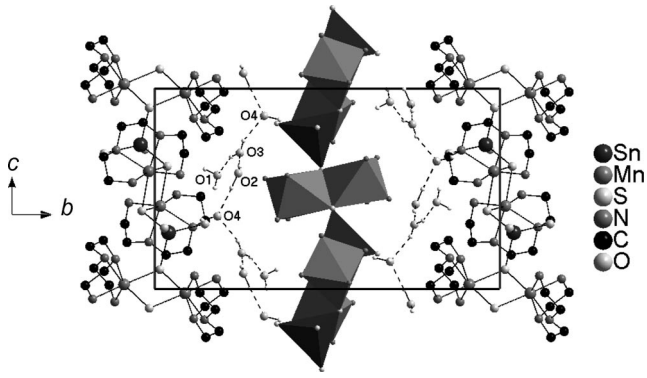

Figure 2. Packing of $[Mn(trien)]_2SnS_4{\cdot}4H_2O$ in the *bc* plane with chains along [001]. H atoms are omitted for clarity and, in the middle chain, the C and N atoms of triethylenetetramine are also omitted for better presentation.

Three water molecules [O(2), O(3), O(4)] are joined by strong hydrogen bonds to form a chain running parallel to the inorganic–organic hybrid compound chain (Figure 2). The last H_2O molecule is attached to the water chain through a O(3)–H···O(1) bond. Several short S···H–N separations (see Table 1) indicate weak hydrogen-bonding interactions between the water molecules and the $\{[Mn(C_6H_{18}N_4)]_2SnS_4\}_\infty$ chain, but there are also some intra- and interchain N–H···S contacts.

We analyzed the binding modes of the chalcogen atoms in chalcogenidostannates; however, the mode found in the title compound has never been observed before.

Experimental Section

Synthesis of $[Mn(trien)]_2SnS_4{\cdot}4H_2O$: Sn (1 mmol; 99.5%, Aldrich), Mn (1 mmol; 99.5%, Alfa Aesar) and S (2.5 mmol) in triethylenetetramine (trien) (2 mL; ≥60%, ABCR) and H_2O (3 mL) were treated in Teflon-lined steel autoclaves (inner volume: 30 mL) for 480 h at 140 °C. The crystalline products were filtered off after the reactions and washed with water and ethanol. Please note that the yield was always lower than 5% despite a broad variation of the synthesis conditions. The compound is neither stable in air nor in vacuo because of the loss of water molecules. The crystals were manually separated, and the homogeneity of the compounds was confirmed by X-ray powder diffraction and CHN analysis: calcd. C 20.0, H 6.2, N 15.5; found C 20.3, H 5.9, N 15.8. Some additional experiments were conducted to evaluate the solubility of the title compound. Crystals were treated with water, ethanol, acetonitrile, or *n*-hexane for 24 h. Whereas the compound is stable in acetonitrile and *n*-hexane, it starts to decompose in water and ethanol. The formerly sharp edges of the crystals became round and the crystal surfaces rough. These observations indicate that the title compound is not stable in polar solvents.

Single Crystal Structure Determination: The intensity data were collected by using a STOE IPDS-1 (Imaging Plate Diffraction System)

with Mo-K_α radiation at 170 K. The structure was solved with direct methods by using the program SHELXS-97,[15] and the refinements were performed against F^2 with SHELXL-97.[16] For all non-hydrogen atoms, anisotropic displacement parameters were used. The hydrogen atoms of the amine were positioned with idealized geometry and refined by using a riding model and a fixed isotropic displacement parameter. The O–H hydrogen atoms were located in the difference map, their bond lengths set to an ideal value, and finally they were refined by using a riding model. Selected refinement results are summarized in Table 2. CCDC-720146 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Selected details of the data collection and structure refinement of the title compound.

	$[Mn(trien)]_2SnS_4\cdot 4H_2O$
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	10.8446(9)
b [Å]	20.9740(10)
c [Å]	13.2746(9)
β [°]	113.487(8)
V [Å^3]	2769.2(3)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.730
μ [mm^{-1}]	2.128
Scan range [°]	$2.28 \leq \theta \leq 28.11$
Reflections collected	15023
Reflections with $F_o > 4\sigma(F_o)$	1472
Independent reflections	6549
Goodness-of-fit on F^2	0.984
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0369, $wR2$ = 0.0854
R indices (all data)	R_1 = 0.0584, $wR2$ = 0.0924
Residual electron density [e Å^{-3}]	0.669/–0.955

Spectroscopic Properties: A MIR spectrum (450–3000 cm^{-1}) was recorded with an ATI Mattson Genesis spectrometer. In the spectrum, the absorptions located at 3437 [m, –NH stretch (asym), –NH_2], 3310, 3294, 3263, 3219, 3181 (s-m, –NH stretch, –NH_2), 3092 (m, –NH stretch), 2908 (s, –CH_2; *m*-s, –NH stretch), 2861 (s, –CH_2; *m*-s, –NH stretch), 1630 (m, –CC), 1565 (s, –NH_2), 1469 (s, –CH, –CH_2), 1389, 1310, 1074, 1050, 1006 (s-m, –CN) cm^{-1} could be assigned to the triethylenetetramine.

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